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10 E. Saturn Blvd.
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06 May 2003

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Greg Drake (AFRL/PRSP) et al., "Structural Effects on the Physical Properties of Ionic Liquids"

5355

**2003 AFOSR Molec Dynamics & Theo Chem Contr Mtg**
**(San Diego, CA, no date provided) (Deadline: 19 May 2003)**

**(Statement A)**

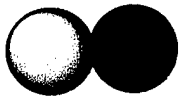
# Structural Effects on the Physical Properties of Ionic Liquids

Greg Drake and Tom Hawkins
AFRL/PRSP
Air Force Research Laboratory
Edwards AFB, CA 93524

and

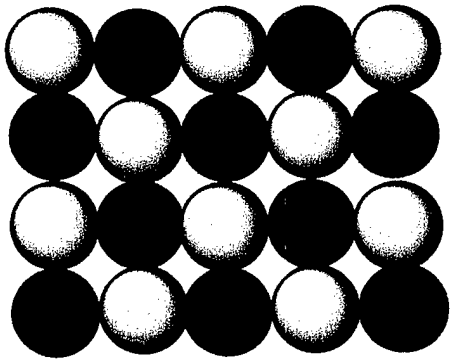
John Wilkes
Department of Chemistry
United States Air Force Academy
USAF Academy, CO 80840

# Ionic Liquids



NOT

versus



Extended lattice

Table salt $Na^+Cl^-$ m.p. = 804 °C Very high

Cryolite $Na_3AlF_6$ m.p. nearly 1000 °C (Hall Process for Al production)

Eutectic of $Li^+Cl^-$ and $K^+Cl^-$ m.p. 355 °C

<u>Molten salts are very hot</u>!

Not commercially viable

Corrosion and energy issues

Giant lattice of miniature magnets stuck together

# Ionic Liquids

**What are Ionic Liquids?**
**A class of salts consisting of cation/anion pair that has a very low melting point.**

**Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.**

**(1) An ionic compound that melts below 100 °C (b.p. of $H_2O$). J. Wilkes, P. Wasserscheid, K. Seddon.**

**(2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.**

**But many of the salts fit both definitions and 2 is really a more specific class of (1).**

# Ionic Liquids

## Important factors affecting the physical properties of ionic liquids

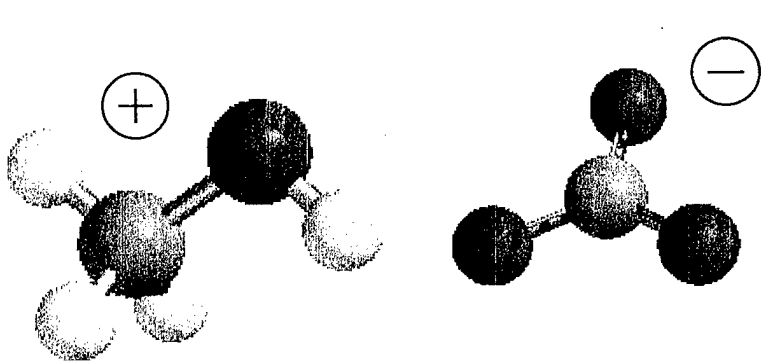
1. Asymmetry of cation as well as anion

2. Packing efficiency

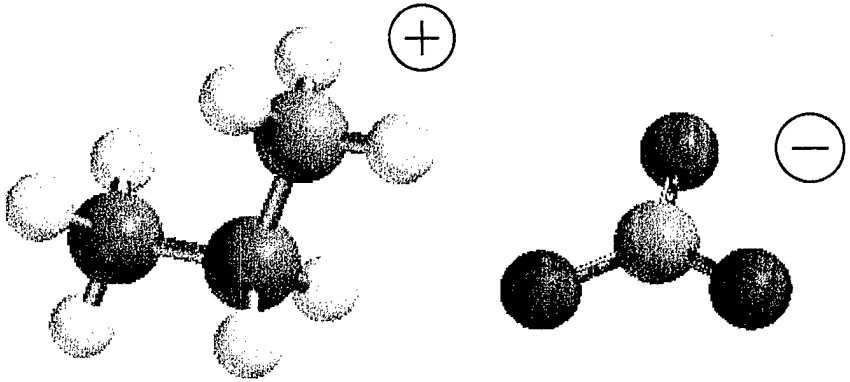
3. Charge delocalization in cationic/anionic species

4. "Sheer size" differentials

# Ionic Liquids



**Hydroxylammonium nitrate (HAN)**
**$[NH_3OH^+][NO_3^-]$m.p. 39-40 °C**

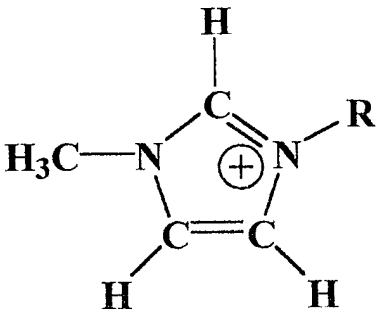


**Ethylammonium nitrate**
**$[CH_3CH_2NH_3^+][NO_3^-]$ m.p. 12 °C**

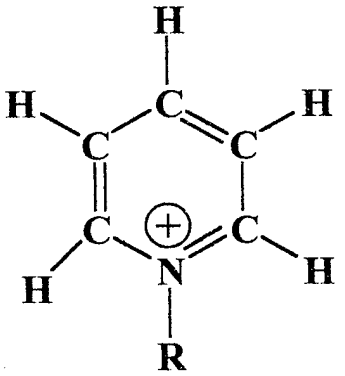
**Serious issues...**
**- can be treacherous**
**- acidic**
**-very hygroscropic**

# Ionic Liquids

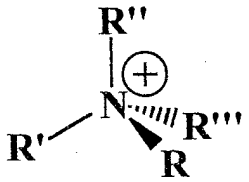
## Some major shapes for organic based cations



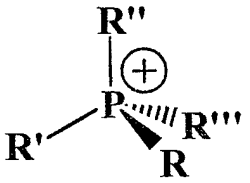

1-methyl-3-alkyl-imidazolium




1-alkylpyridinium




Tetralkylammonium




Tetralkylphosphonium

# Ionic Liquids

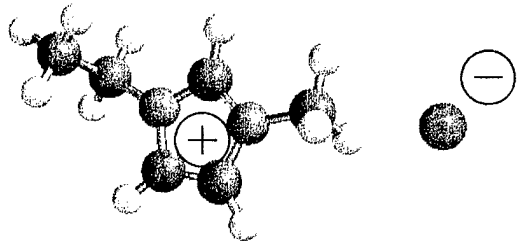
**The group of anions for ionic liquids is much larger and growing....**

| water soluble | water insoluble |
|---|---|
| $CH_3CO_2^-$ | $PF_6^-$ |
| $CF_3CO_2^-$ | $[BR_1R_2R_3R_4]^-$ |
| Cl-, Br-, I- | $[(CF_3SO_2)_2N]^-$ |
| $NO_3^-$ | $BF_4^-$ |
| $BF_4^-$ | $R\text{-}SO_3^-$ |
| $NO_2^-$ | |
| $[AlCl_4^-, Al_2Cl_7^-]$ | |

**Typically R groups are n-alkyl groups**
**This list is not comprehensive but it covers the majority of what is out there.**

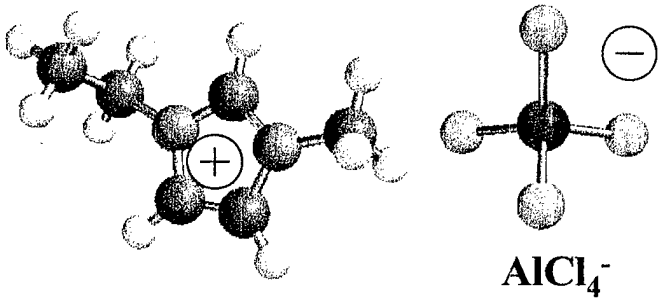
# Ionic Liquids

**Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as $AlCl_3$ and $Cl^-$ have an equilibrium based on their respective concentrations.**



**"Basic"**

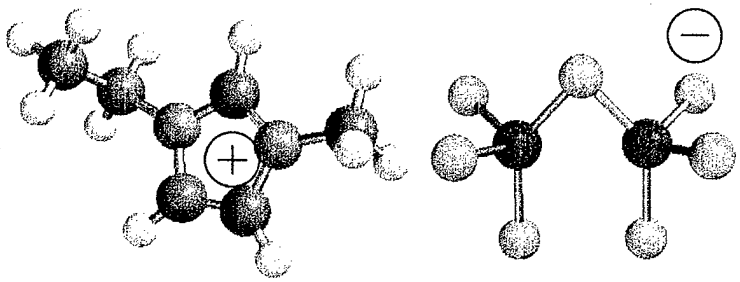
$AlCl_3$



$AlCl_4^-$

**"Neutral"**

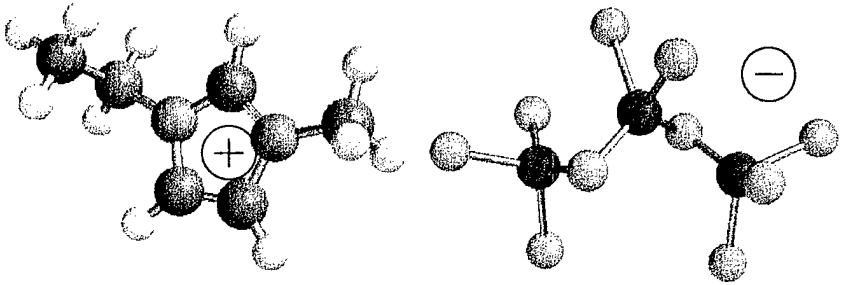
$AlCl_3$



$Al_2Cl_7^-$

**"Acidic"**

$AlCl_3$

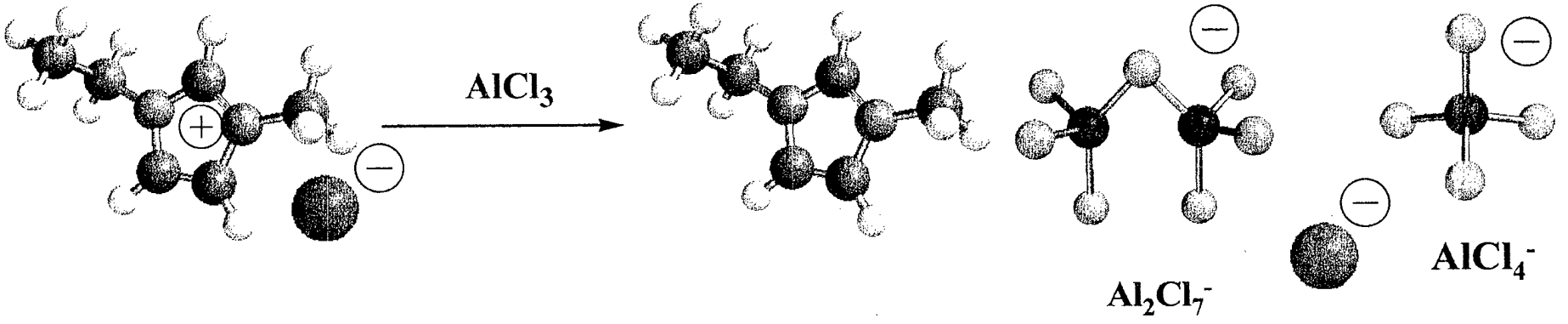


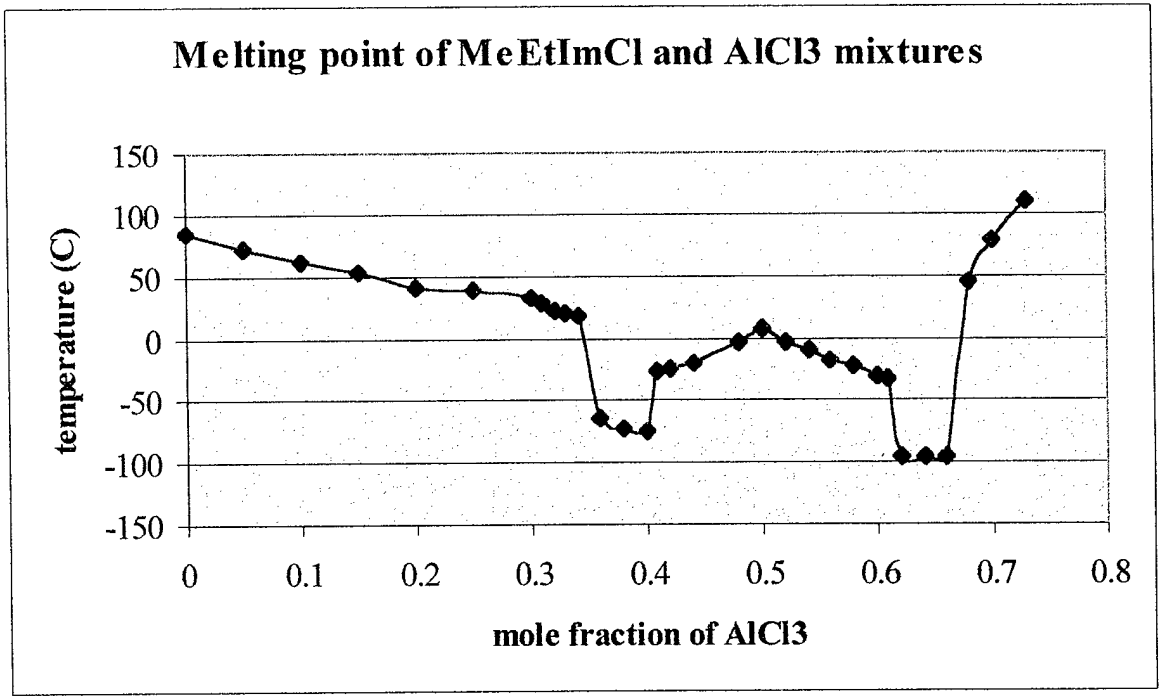
$Al_3Cl_{10}^-$

**"Strongly acidic"**

Wilkes, J. S. Green Chemistry **2002**, *4*, 3.

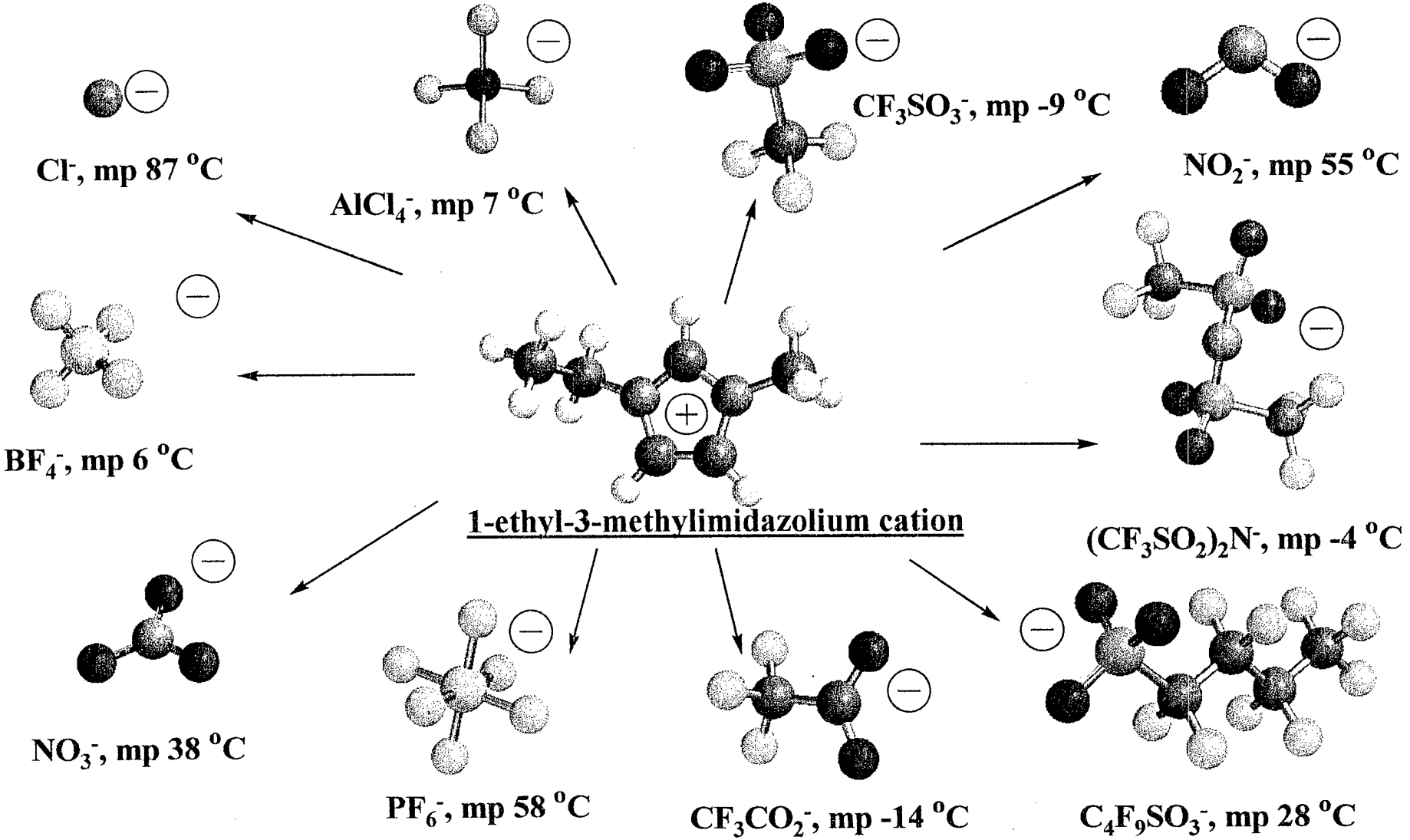
# Ionic Liquids



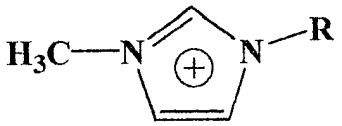

Fannin, A. ; Floreani, D. ; King, L. ; Landers, J. ; Piersma, B. ; Stetch, D. ; Vaughn, R. ; Wilkes, J. ; Williams, J. J. Phys. Chem. **1984**, 88, 2614.

# Ionic Liquids



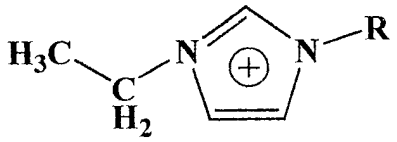

Wasserscheid, P.; Keim, W. Angew. Chem. Int. Ed. Engl. **2000**, 39, 3772. Wasserscheid, P, Welton, T. (eds.) Ionic Liquids in Synthesis Wiley-VCH, FRG, **2003**
.Seddon, K.R. ; Holbrey, J. D. Clean Products and Processes **1999**, 1, 223. Rogers, R.; Seddon, K. (eds.) Ionic Liquids A.C.S. Symp. Ser. 818 2002 A.C.S Publ. Co.

# Ionic Liquids melting points



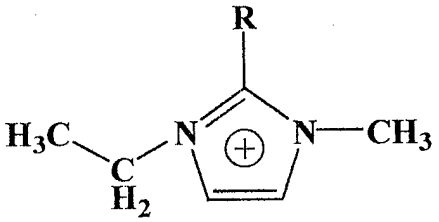
3-methyl-1-R-imidazolium

| Substituent | Triflate (m.p.) | Bis(trifluorosulfonamide) m.p. |
|---|---|---|
| 1-methyl | 39 | 22 |
| 1-ethyl | -9 | -3 |
| 1-butyl | 16 | -4 |
| 1-$CH_2OCH_2CH_3$ | 27 | <-30(Tg) |
| 1-$CH_2$-$CF_3$ | 45 | <-30(Tg) |



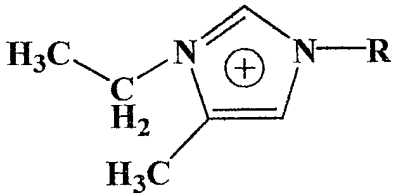
3-ethyl-1-R-imidazolium

| Substituent | Triflate (m.p.) | Bis(trifluorosulfonamide) m.p. |
|---|---|---|
| 1-ethyl | 23 | 14 |
| 1-butyl | 2 | <-30(Tg) |



1-ethyl-2-R-3-methyl-imidazolium

| Substituent | Triflate (m.p.) | Bis(trifluorosulfonamide) m.p. |
|---|---|---|
| 2,3-dimethyl | 109 | 20 |
| 2-ethyl-3-methyl | 113 | 28 |

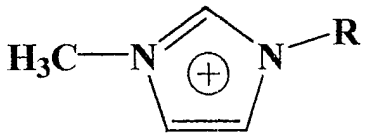


1-ethyl-3-R-5-methyl-imidazolium

| Substituent | Triflate (m.p.) | Bis(trifluorosulfonamide) m.p. |
|---|---|---|
| 3-methyl | 6 | -3 |
| 3-ethyl | 35 | -22 |

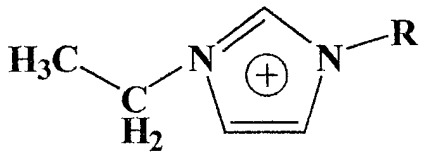
Bonhote, P. ; Diaz, A. ; Papageorgiou, N. ; Kalyanasundaram, K. ; Gratzel, M. Inorg. Chem. **1996**, *35*, 1168.

# Ionic Liquids



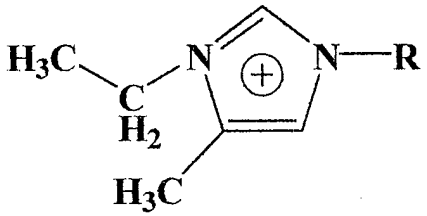
3-methyl-1-R-imidazolium

| Bis(trifluoromethylsulfonamide) | η(cP) | Λ(mS/cm) |
|---|---|---|
| 1-methyl | 44 | 8.4 |
| 1-ethyl | 34 (45) | 8.8 (8.6) |
| 1-butyl | 52 (90) | 3.9 (3.7) |
| 1-$CH_2OCH_2CH_3$ | 54 (74) | 4.2 (3.6) |
| 1-$CH_2$-$CF_3$ | 248 | 0.98 |



3-ethyl-1-R-imidazolium

| Bis(trifluoromethylsulfonamide) | η(cP) | Λ(mS/cm) |
|---|---|---|
| 1-ethyl | 35 (53) | 8.5 (7.5) |
| 1-butyl | 48 | 4.1 |



1-ethyl-3-R-5-methyl-imidazolium

| Bis(trifluoromethylsulfonamide) | η(cP) | Λ(mS/cm) |
|---|---|---|
| 3-methyl | 37 (51) | 6.6 (6.4) |
| 3-ethyl | 36 | 6.2 |

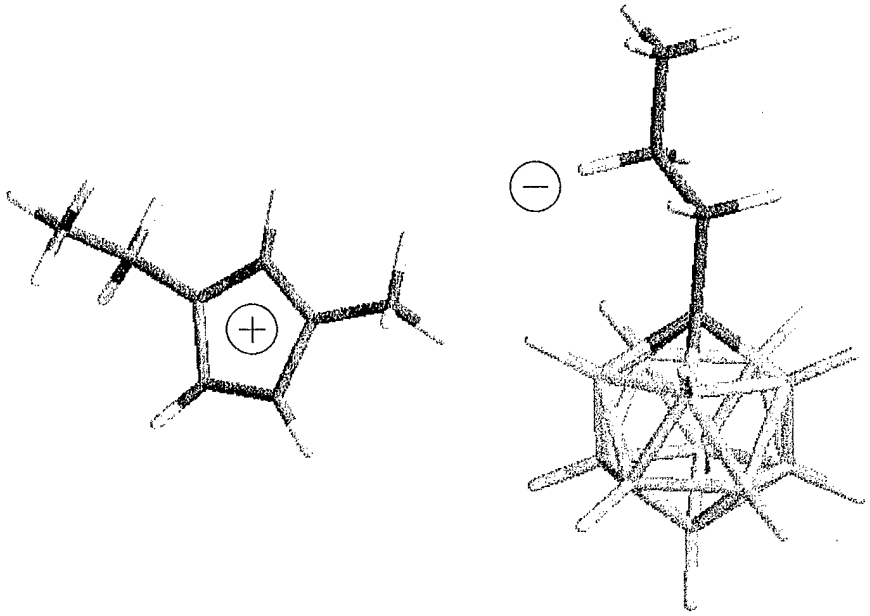
Red values in () are for corresponding $CF_3SO_3$- salt

**Viscosity and conductivity increase with increasing chain length but intramolecular hydrogen bonding can be important. Size and "charge" of anion also significant.**

Bonhote, P. ; Diaz, A. ; Papageorgiou, N. ; Kalyanasundaram, K. ; Gratzel, M. Inorg. Chem. **1996**, *35*, 1168.

# Ionic Liquids

**The end extreme of non-coordinating anions has been achieved through the use of carborane anion in the formation of ionic liquids. Essentially no hydrogen bonding.**

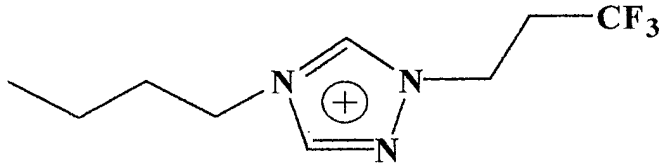


| Ionic liquid | m.p. °C |
|---|---|
| [EMIM][$HCB_{11}H_{11}$] | 122 |
| [EMIM][1-$CH_3$-$CB_{11}H_{11}$] | 59 |
| [EMIM][1-$CH_2CH_3$-$CB_{11}H_{11}$] | 64 |
| [EMIM][1-$CH_2CH_2CH_3$-$CB_{11}H_{11}$] | 45 |
| [EMIM][1-$CH_2CH_2CH_2CH_3$-$CB_{11}H_{11}$] | 49 |

**1-ethyl-3-methyl-imidazolium icosahedral**
**1-propyl-1-carborane [EMIM][1-prop-$CB_{11}H_{11}$]**

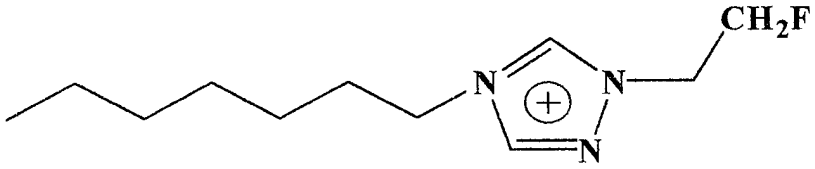
Larsen, A. S. ; Holbrey, J. D.; Tham, F. S.; Reed, C. A. J. Amer. Chem. Soc. **2000**, *122*, 7264.

# Ionic Liquids



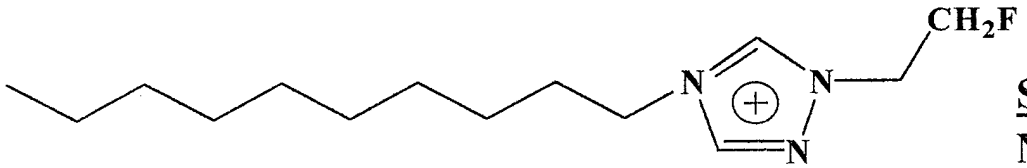
1-(3',3',3'-trifluoro-n-propyl)-3-n-butyl-1,2,4-triazolium

| Salt | m.p.(°C) | DSC onset (°C) |
|---|---|---|
| $NTf_2^-$ | -67 | 395 |
| $TfO^-$ | 33 | 379 |



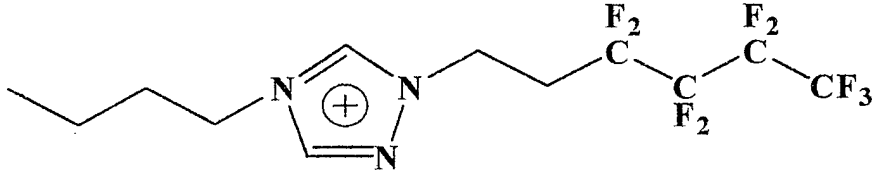
1-(2'-fluoroethyl)-3-n-heptyl-1,2,4-triazolium

| Salt | m.p.(°C) | DSC onset (°C) |
|---|---|---|
| $NTf_2^-$ | -70 | 359 |
| $BF_4^-$ | 52 | 336 |



1-(2'-fluoroethyl)-3-n-decyl-1,2,4-triazolium

| Salt | m.p.(°C) | DSC onset (°C) |
|---|---|---|
| $NTf_2^-$ | -62 | 426 |
| $TfO^-$ | 46 | 362 |



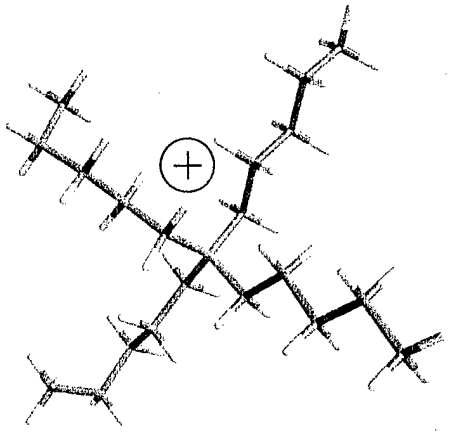
1-(1H,1H,2H,2H-perfluoro-n-hexyl)-3-n-butyl-1,2,4-triazolium

| Salt | m.p.(°C) | DSC onset (°C) |
|---|---|---|
| $NTf_2^-$ | 69 | 394 |
| $TfO^-$ | 173 | 391 |
| $PF_6^-$ | 296 | 357 |

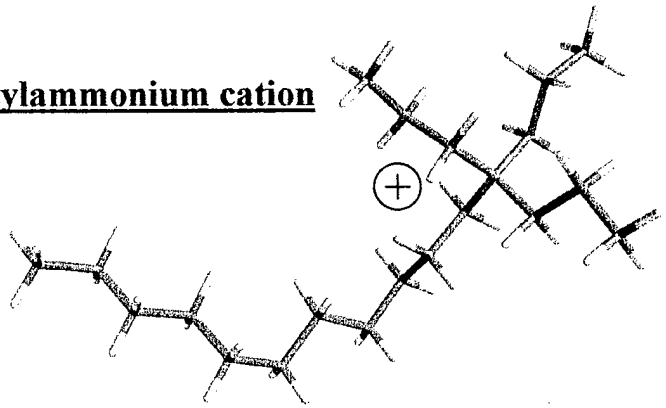
Mirzaei, Y. R. ; Twamley, B. ; Shreeve, J. M. J. Org. Chem. **2002**, *67*, 9340.

# Ionic Liquids

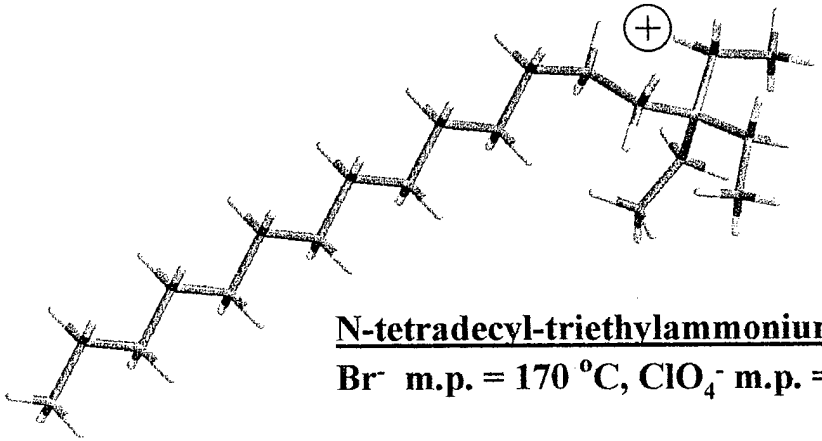
**Substituted ammonium salts $R_4N^+X^-$ Variations in melting point based on cation structure.**



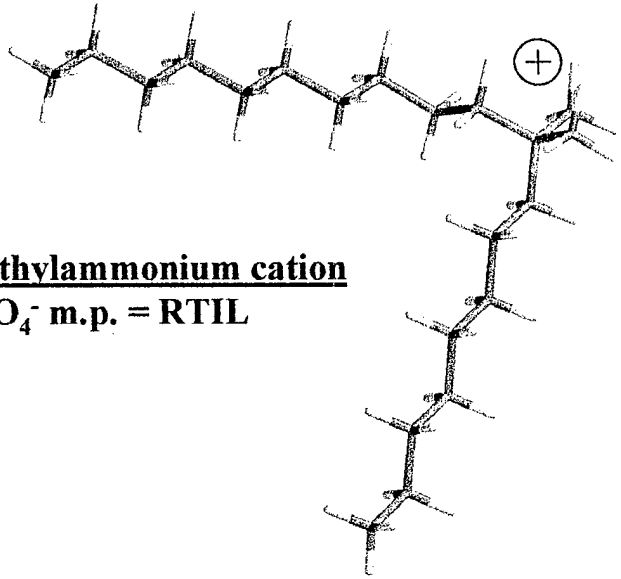
**Tetra-n-pentylammonium cation**
**$Br^-$ m.p. = 101 °C**
**$ClO_4^-$ m.p. = 118 °C**



**Tris-(n-propyl)-undecylammonium cation**
**$Br^-$ m.p. = 67 °C**
**$ClO_4^-$ m.p. = 65 °C**



**N-tetradecyl-triethylammonium cation**
**$Br^-$ m.p. = 170 °C, $ClO_4^-$ m.p. = 152 °C**



**N-decyl-n-octyl-dimethylammonium cation**
**$Br^-$ m.p. = RTIL, $ClO_4^-$ m.p. = RTIL**

Gordon, J. E. ; SubbaRao, G. N. J. Amer. Chem. Soc. **1978**, *100*, 7445.

# Ionic Liquids

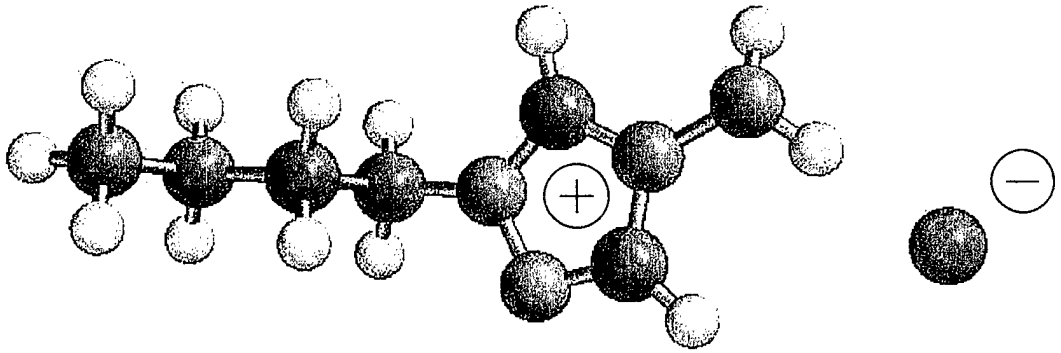
**Substituted ammonium salts $[R_4N^+][X^-]$Recently work has been done by using more desirable anions.**

| Substituted Ammonium Salt | M.P. (° C) | Density ($g/cm^3$) | Viscosity (cp) | $\Lambda$ ($\Omega^{-1}$ $cm^2$/mole) |
|---|---|---|---|---|
| $[(n\text{-}C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$ | -74 (g) | 1.33 | 153 | 1.4 |
| $[(n\text{-}C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$ | -73 (g) | 1.28 | 153 | 1.4 |
| $[(n\text{-}C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$ | -73(g) | 1.27 | 181 | 1.3 |
| $[(n\text{-}C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$ | 20 | 1.27 | 167 | 2.5 |
| $[(n\text{-}C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$ | -79 | 1.26 | 75 | 1.9 |
| $[(n\text{-}C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$ | -74 | 1.25 | 202 | 1.3 |
| $[(n\text{-}C_6H_{13})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$ | 26 | 1.15 | 595 | 0.8 |
| $[(n\text{-}C_7H_{15})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$ | -67 | 1.17 | 606 | 0.8 |
| $[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$ | -63 | 1.12 | 574 | 0.7 |
| $[(n\text{-}C_7H_{15})(Et)_3(ipr)_2N^+][N(SO_2CF_3)_2^-]$ | -82 | 1.27 | 362 | 1.2 |
| $[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][OSO_2CF_3^-]$ | -57 | 1.02 | 2030 | 0.07 |

**-most have very low glass points**
**-densities decrease as expected**
**-viscosity increases dramatically with increasing alkyl length**
**-conductivity decreases with cation size (mobility issue)**

Sun, J. ; Forsyth, M. ; MacFarlane, D. R. J. Phys. Chem. B **1998**, *102*, 8858.

# Ionic Liquids

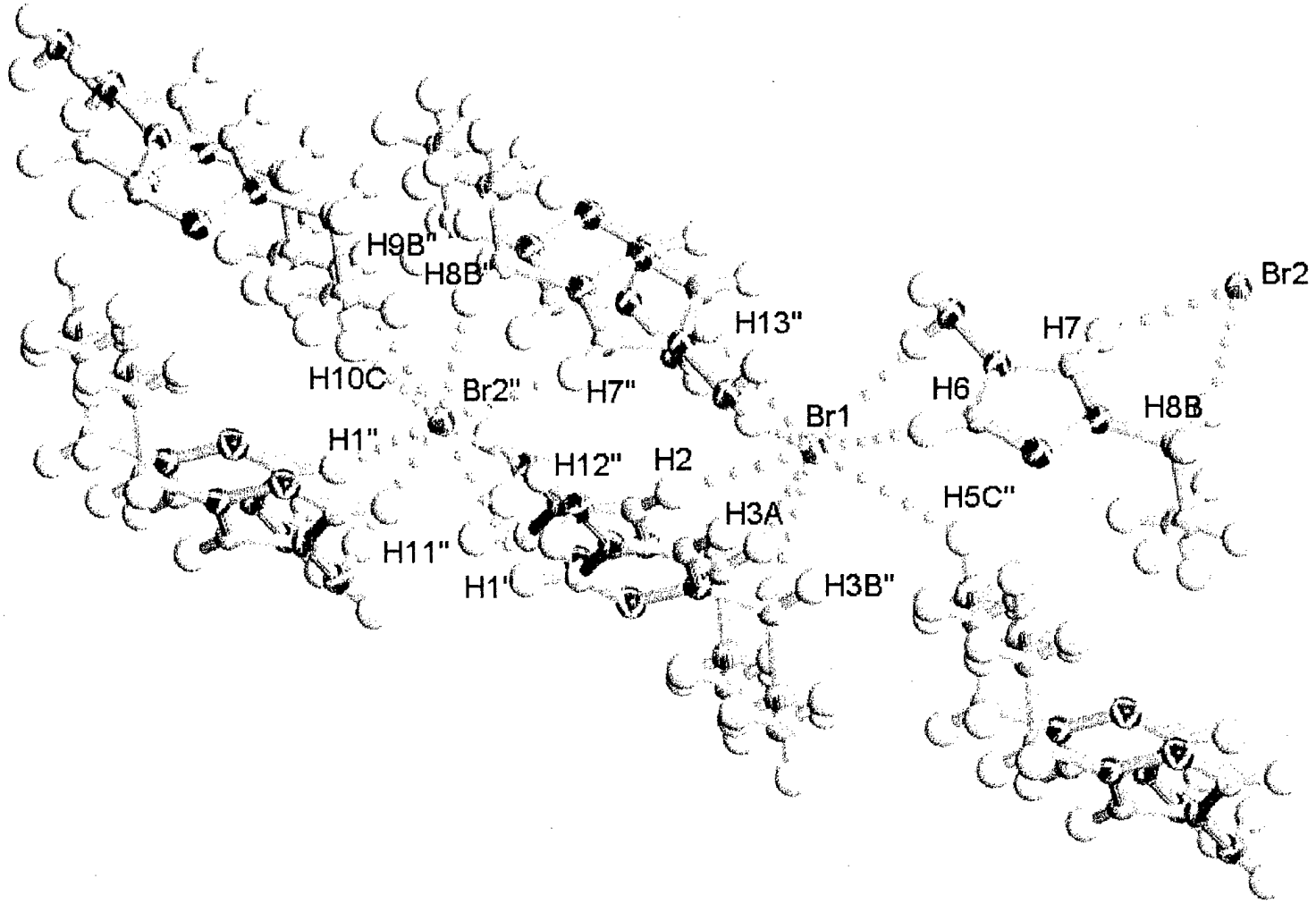


**1-n-butyl-4-amino-1,2,4-triazolium bromide**

| 1-substituted 4AT salts | m.p. (°C) | dec. onset (°C) | density (g/cm$^3$) |
|---|---|---|---|
| 1-ethyl | 63° | 110 | 1.69 |
| 1-n-propyl | 60° | 120 | 1.56 |
| 1-isopropyl | 90° | 110 | 1.60 |
| 1-butyl | 48° | 130 | 1.46 |
| 1-n-pentyl | 54° | 130 | 1.37 |
| 1-n-hexyl | 76° | 120 | 1.34 |
| 1-n-heptyl | 94° | 120 | 1.30 |
| 1-n-octyl | 80° | 135 | 1.27 |
| 1-n-nonyl | 81° | 140 | 1.26 |
| 1-n-decyl | 90° | 135 | 1.23 |

[#]Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

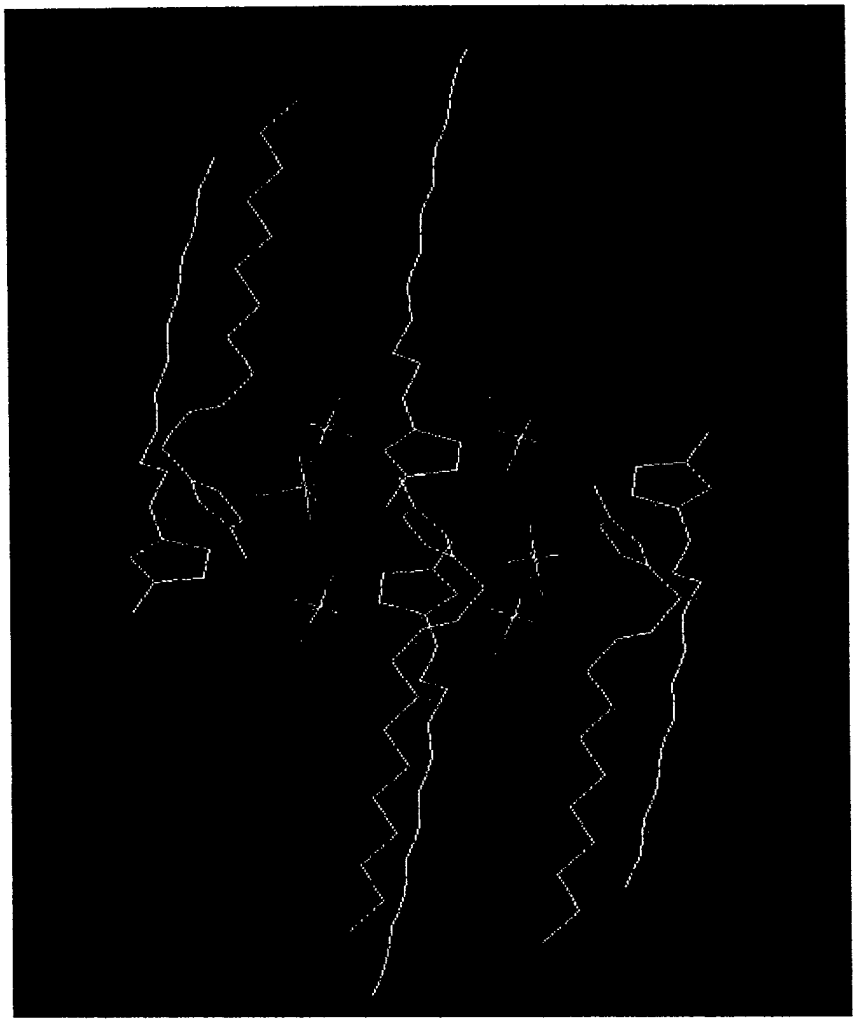
# Ionic Liquids



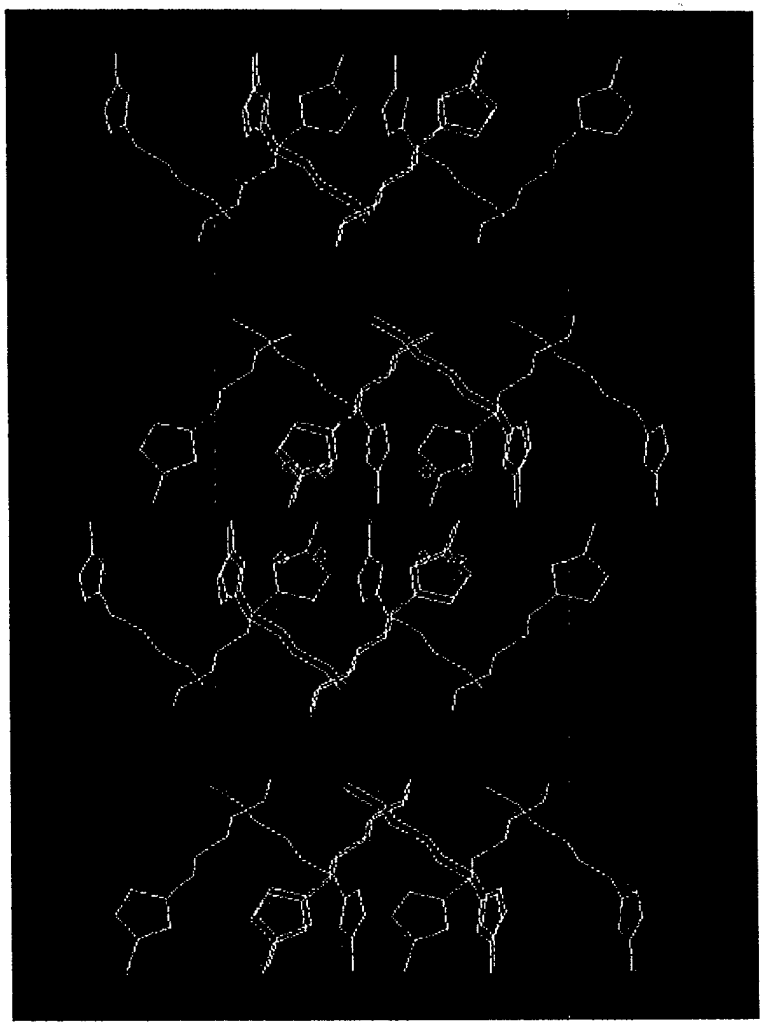

**Extensive hydrogen bonding in 1-n-propyl-4-amino-1,2,4-triazolium bromide**

[#]Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

# Ionic Liquids



**1-dodecyl-3-methylimidazolium hexafluorophosphate***



**1-hexyl-4-amino-1,2,4-triazolium bromide#**

*Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. J. Mater. Chem. **1998**, *8*, 2627.

#Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

# Ionic Liquids

## Summary and Conclusions

- Overall cation symmetry or lack thereof dramatically affects the physical properties of ionic liquids.

- Inter- as well as intra- molecular interactions especially hydrogen bonding are very important.

- Conductivity and viscosity are indirectly related, and both are significantly affected by the size and charge distribution of the cation and/or anion.

- New classes of ionic liquids are appearing and the field has tremendous promise for new and exciting breakthroughs.

# Ionic Liquids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